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Iron(IV)phthalocyanines. Magnetic and Spectral Features of μ-Nitrido-iron-phthalocyanine, $(FePc)_2N$ and of some Oxidized Derivatives

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As part of a wider study of iron(III)phthalocyanine complexes [1–6] we report here preliminary data on the electronic features of the binuclear complex μ-nitrido(phthalocyaninato)iron, $(FePc)_2N$, and of some of its oxidized derivatives. Comparisons are made with the tetraphenylporphyrin analog, $(FeTPP)_2N$, the electronic features of which have been probed in great detail [7, 8]. While the present study was in progress, Ercolani and coworkers also reported the isolation of $(FePc)_2N$, prepared by a different method to that described here, together with the electrochemical properties of the complex [9, 10].

Experimental

Synthesis of $(FePc)_2N$

119 mg (0.1 mmol) of $(PNP)[Fe(N_3)_2Pc(2-)]$** [1, 11] were heated at 210 °C in a vacuum in a platinum crucible. The decomposition began at about 170 °C. The starting crystals softened and produced a foam-like mass following the evolution of gas, which on cooling was washed repeatedly with dichloromethane. The reddish-blue finely crystalline product was dried *in vacuo*.

The complex can also be synthesized from the azido derivative of the oxidized phthalocyanine iron(III) complex, $[Fe(N_3)_2Pc(1-)]0.25I_2$. This dark brown–black starting material [11] decomposes spontaneously and vigorously at 65 °C to yield the red–blue μ-nitrido complex. The conversion also occurs using a suspension of the azido complex in ethyleneglycol dimethyl ether. *Anal.* Found: C, 66.8; Fe, 9.7. Calc. for $C_{64}H_{32}Fe_2N_{17}$: C, 66.8; Fe 9.7%.

Synthesis of $[(XFePc)_2N]X$, where X = Br, NO_3, CF_3CO_2

A typical preparation is as follows for the X = Br complex. 57.5 mg (0.05 mmol) of $(FePc)_2N$ in 5 ml of CH_2Cl_2 were reacted with an excess of Br_2 in CH_2Cl_2. The dark brown product was centrifuged off and washed repeatedly with CH_2Cl_2 before being dried in vacuum. *Anal.* Found: C, 55.0; Fe, 8.0; Br, 17.1. Calc. for $C_{64}H_{32}Fe_2N_{17}Br_3$: C, 55.3; Fe, 8.0; Br, 17.2%. Found for $X = NO_3^-$: C, 57.3; Fe, 8.3. Calc. for $C_{64}H_{32}Fe_2N_{19}O_9$: C, 57.5; Fe, 8.3%.

Physical Measurements

These were made as described previously [1].

Results and Discussion

$(FePc)_2N$ is formed by thermal degradation of the bis-azido iron(III)phthalocyanine derivatives $(PNP)[Fe(N_3)_2Pc]$ or $[Fe(N_3)_2Pc(1-)]0.25I_2$ [1, 11]. This is related to the method used by Ercolani *et al.* [9, 10] in which $FePc(2-)$ was suspended in boiling α-chloronaphthalene and reacted with excess sodium azide. It is probable that intermediate azido species were also formed in this heterogeneous oxidation reaction. The IR spectra of the present samples of $(FePc)_2N$ are very similar to the one reported by Ercolani *et al.* [10] with a strong band at 913 cm^{-1} being due to the Fe–N–Fe antisymmetric stretching frequency. However, we have noted that the intensity of this band varies from preparation to preparation and in some cases splitting of the band occurs. There are no bands at ~1460 and ~1360 cm^{-1} characteristic of the radical cation $Pc(1-)$ ligand [12], and so the complex can be represented by $(FePc(2-))_2N$. The Q-band at 690 nm in the visible spectrum shifts to 630 nm when the complex dissolves in N-bases such as pyridine, ethylenediamine or imidazole/CH_2Cl_2 to form blue-coloured solutions. This spectral shift is characteristic of axial coordination of the N-base occurring as in the related $(FePc)_2O$ system [6].

Axial coordination of anionic ligands such as X = halide$^-$, CN^-, NCO^- has also been observed in complexes of the type $(TBA)[(XFePc)_2N]$ formed by reacting $(FePc)_2N$ in CH_2Cl_2 with the tetrabutylammonium salt (TBA)X. Some of these products are highly crystalline and efforts are continuing to obtain crystals suitable for X-ray diffraction studies since the structure of the parent $(FePc)_2N$ is not yet known. Further details will be published separately.

Axial coordination, as well as oxidation, occurs when $(FePc)_2N$ is reacted in dichloromethane with oxidants such as bromine, trifluoroacetic acid or concentrated nitric acid to produce the red–brown coloured compounds $[(BrFePc(1-))_2N]Br$, $[(CF_3CO_2)FePc(1-))_2N](CF_3CO_2)$ and $[((NO_3)FePc(1-))_2N]NO_3$. The latter is a rather rare compound since concentrated nitric acid normally bleaches Fe(III)Pc compounds colourless. The IR spectra in

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**PNP^+ = bis(triphenylphosphine) nitrogen$^+$ cation.

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TABLE I. Magnetic and Spectral Data

Compound[a]	Temperature (K)	δ[b] (mm s^{-1})	ΔE_Q (mm s^{-1})	$\bar{\mu}$ (μ_B at 295 K)	ESR g value (77 K)	Reference
$(FePc(2-))_2N$	4.2	0.06	1.78	2.33	2.13, 2.05	this work
$[(BrFePc(1-))_2N]Br$	4.2	−0.08 −0.10	1.74 (65%) 2.02 (35%)	2.34	v. br (+ weak g = 2.0 radical)	this work
$[(CF_3CO_2)FePc(1-))_2N](CF_3CO_2)$	4.2	−0.10	1.82	1.98	2.0	this work
$(FeTPP)_2N$	131	0.18	1.08	2.04	2.15, 2.01	13
$[(FeTPP)_2N]SbCl_6$	126	0.01	1.94			13
$[(FeTPP)_2N](SbCl_6)_2$	126	0.07 −0.04	1.48 (50%) 2.21 (50%)	2.0	2.0[c]	13

[a] Neat solid samples were used in the present work. [b] Relative to Fe metal at room temperature. [c] Resolvable into three g values.

the range 1700–500 cm^{-1} of these oxidized species are different in overall shape to that of $(FePc(2-))_2N$, with bands occurring at 1350 and 1459 cm^{-1} due to the π-radical cation ligand, Pc(1−). Interestingly there is only a very weak band at 908 cm^{-1} in the region expected for ν_{as}(Fe–N–Fe). The present oxidized species can be regarded as further oxidized derivatives of a one-electron oxidized complex such as $[(pyFePc(2-))_2N]PF_6$, briefly described by Ercolani *et al.* [9, 10].

The magnetic and spectral features of $(FePc(2-))_2N$ and of $[XFePc(1-)_2N]X$ ($X = Br^-$, $CF_3CO_2^-$) are given in Table I and are compared with data for related μ-nitrido–FeTPP systems. The Mössbauer parameters are particularly useful for assigning formal oxidation states to Fe in these compounds. By analogy to $[(FeTPP)_2N]^{z+}$ ($z = 1, 2$) and other Fe(IV) porphyrins, $(FePc(2-))_2N$ and $(XFePc(1-))_2N]X$ complexes all show δ values symptomatic of predominant Fe(IV) character. The δ value for $(FePc(2-))_2N$ (Fig. 1) is slightly more positive than it is for its oxidized derivatives but less positive than for $(FeTPP)_2N$. Since only one Mössbauer doublet is observed at 4.2 K, the Fe sites in $(FePc(2-))_2N$ are equivalent, indicative of either $Fe^{(3.5)+}$ behaviour resulting from delocalized $Fe^{III}Pc(2-)$–N=$Fe^{IV}Pc(2-)$ forms, as found in $(FeTPP)_2N$, or from Fe^{IV} behaviour in $Fe^{IV}Pc(2-)$=N=$Fe^{IV}Pc(2-)$ in which the unpaired electron is more associated with the bridging nitrogen. The ESR spectrum at 77 K of solid $(FePc(2-))_2N$ is indicative of one electron per molecule and is just resolvable into two g values. The lines do not display N-hyperfine structure, probably because of exchange broadening effects*. The magnetic moment of the complex is also indicative of a ground state with one unpaired spin although $\bar{\mu}$ is a little higher in size than for $(FeTPP)_2N$. It decreases markedly from 2.33 μ_B at 295 K to 1.36 μ_B at 4.2 K which is suggestive of intramolecular, or perhaps intermolecular, spin coupling occurring.

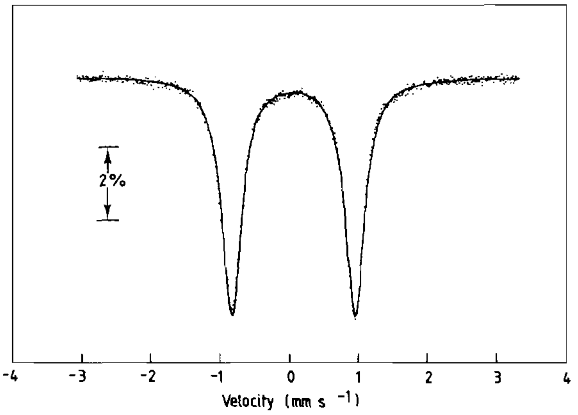

Fig. 1. Mössbauer spectrum of $(FePc)_2N$ at 4.2 K in zero-field.

The oxidized species clearly contain Fe(IV) in view of their negative isomer shift values. In the case of $[(BrFePc(1-))_2N]Br$ the Mössbauer spectrum appears to be a single doublet but can be best fitted to two doublets (Table I). This could be indicative of two slightly different Fe(IV) environments. A more pronounced separation of doublets was reported in the case of $[(FeTPP)_2N](SbCl_6)_2$ and was ascribed to localization of the porphyrin TPP(1−) radical at one end of the dimer [13]. The magnetic moments and ESR spectra of $[BrFePc(1-))_2N]Br$ and $[((CF_3CO_2)FePc(1-))_2N](CF_3CO_2)$ generally, although not entirely, point to a $S = 1/2$ ground state. This is rather difficult to justify in view of the most probable valency formalism, $[(X)Fe^{IV}Pc(1-)$–N=$Fe^{IV}Pc(1-)(X)]^+$, deduced from the Mössbauer and IR data. It is desirable to obtain crystal structure information and variable temperature magnetic data in order to fully characterize these oxidized μ-nitrido species. The spin-state on the individual Fe(IV) centres is most likely to be $S = 1$, but this needs to be confirmed by applied field Mössbauer measurements [14, 15].

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*This is similar to the situation in $(FeTPP)_2N$ in which ^{14}N-hyperfine splitting was resolved only when dilute thin films were prepared in CS_2 [7].

In conclusion, we have shown that $(FePc(2-))_2N$ has rather similar electronic properties to $(FeTPP)_2N$ with more pronounced Fe(IV) character in the case of the phthalocyanine complex. Air stable iron(IV) phthalocyanine radical cations are obtained on oxidation of $(FePc(2-))_2N$ with oxidants such as Br_2, CF_3COOH and HNO_3. The structural and electronic properties of these compounds, and of their porphyrin counterparts [13] will prove useful in understanding similar species in hydroperoxidase enzymes [16].

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